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(54) (Modified) Hydrogenated diene block copolymer and composition comprising the same

(Modifiziertes) hydriertes Dien-Blockcopolymer und dieses enthaltende Zusammensetzung

Copolymère séquéncé de diène hydrogéné (modifié) et composition le contenant

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Description

[0001] This invention relates to a special hydrogenated block copolymer. More particularly, this invention relates to a (modified) hydrogenated diene block copolymer which is pelletizable by itself and has excellent processability and further has excellent weather resistance, impact resistance and paintability (peeling resistance) and which can suitably provide a composite system with improved impact resistance, paintability (peeling resistance), adhesion and flexibility, as well as to a composition comprising the (modified) hydrogenated diene block copolymer.

[0002] Diene copolymers having double bond unsaturations in the molecule are inferior in thermal stability, weather resistance and ozone resistance. As the method for improving these properties, there are known methods comprising hydrogenating the double bond unsaturations. These methods are disclosed in, for example, Japanese Patent Publication Nos. 43-19960, 45-39275 and 48-3555 and Japanese Patent Application Kokai Nos. 56-62805 and 59-133203. The hydrogenated polymers obtained by the methods disclosed in the above documents have heat resistance and ozone resistance as desired and are in wide use for modification of resin and other uses.

[0003] Other hydrogenated polymers are disclosed in, for example, Japanese Patent Publication Nos. 63-14721 and 48-30151.

[0004] Also, ethylene- α -olefin copolymers, etc. are known as a polymer having excellent heat resistance and weather resistance.

[0005] These polymers, however, are insufficient for blending with a non-polar resin or a polar resin to obtain a composition well balanced in impact resistance and moldability.

[0006] The present inventors have made study on hydrogenated polymers and, as a result, found that a particular hydrogenated diene block copolymer can solve the above-mentioned technical problem of the prior art.

[0007] An object of this invention is to provide a (modified) hydrogenated block copolymer which can be easily pelletized to give pellets with improved blocking resistance, which has excellent heat resistance, weather resistance and ozone resistance, and which when used as a modifier for other resins, can improve their properties in low temperature impact resistance, weather resistance, paintability (peeling resistance), flexibility and ozone resistance.

[0008] Another object of this invention is to provide a composition of improved properties, comprising (1) a (modified) hydrogenated diene block copolymer and (2) a non-polar resin and/or a polar resin.

[0009] According to this invention, there is provided a hydrogenated diene block copolymer having a polyester-reduced number-average molecular weight of 50,000-600,000 which is a hydrogenation product of an (A)-(B) block copolymer in which (A) means an alkenyl aromatic compound polymer block [hereinafter referred to as "Block (A)"] and (B) means an alkenyl aromatic compound-conjugated diene random copolymer block wherein the vinyl content of the conjugated diene portion is more than 60% [hereinafter referred to as "Block (B)"], an (A)-(B)-(C) block copolymer in which (A) means Block (A), (B) means Block (B) and (C) means an alkenyl aromatic compound-conjugated diene copolymer tapered block wherein the proportion of the alkenyl aromatic compound increases gradually [hereinafter referred to as "Tapered Block (C)"], or an (A)-(B)-(A) block copolymer in which (A) means Block (A) and (B) means Block (B), in which block copolymer

(1) the weight proportion of the alkenyl aromatic compound/the conjugated diene is 5/95 to 60/40, and

(2) the content of the bound alkenyl aromatic compound in at least one Block (A) is at least 3% by weight and the total of the bound alkenyl aromatic compound contents in two Block (A)'s or Block (A) and Tapered Block (C) is 3-50% by weight based on the total monomers, and in which hydrogenation product at least 80% of the double bonds of the conjugated diene portion are saturated by the hydrogenation.

[0010] In another aspect, the present invention provides a hydrogenated diene block copolymer having a polystyrene-reduced number-average molecular weight of 100,000-600,000 which is a hydrogenation product of an (A)-(B) block copolymer consisting of (A) an alkenyl aromatic compound polymer block and (B) an alkenyl aromatic compound-conjugated diene random copolymer block, an (A)-(B)-(C) block copolymer consisting of the block (A), the block (B) and (C) an alkenyl aromatic compound-conjugated diene copolymer tapered block wherein the proportion of the alkenyl aromatic compound increases gradually, or an (A) - (B)-(A) block copolymer consisting of the block (A), the block (B) and the block (A), in which block copolymer

(1) the weight proportion of the alkenyl aromatic compound/the conjugated diene is 5-40/95-60,

(2) the total of the bound alkenyl aromatic compound contents in the block (A) and the block (C) or the two blocks (A) is 3-25% by weight based on the total monomers and the content of the bound alkenyl aromatic compound in at least one block (A) is at least 3% by weight, and

(3) the vinyl content in the conjugated diene portion in the block (B) is more than 60%, and in which hydrogenation copolymer at least 90% of the double bonds of the conjugated diene portion are saturated.

References hereinafter to a hydrogenated diene block copolymer relate to the hydrogenated diene block copolymer of either aspect of the invention.

[0011] This invention also provides a modified hydrogenated diene block copolymer obtained by modifying 100 parts by weight of the above-mentioned hydrogenated diene block copolymer with 0.01-20 parts by weight of an unsaturated compound having at least one functional group selected from the group consisting of acid anhydride group, carboxyl group, hydroxyl group, amino group and epoxy group.

[0012] This invention further provides a hydrogenated diene block copolymer composition comprising 1-99% by weight of the above hydrogenated diene block copolymer (I) and/or modified hydrogenated diene block copolymer (I) [hereinafter these are generically referred to as "(modified)hydrogenated diene block copolymer"] and 99-1% by weight of a non-polar resin (II) and/or a polar resin (III).

[0013] The alkenyl aromatic compound used in the hydrogenated diene block copolymer of this invention includes styrene, tert-butylstyrene, α -methylstyrene, p-methylstyrene, divinylbenzene, 1,1-diphenylstyrene, N,N-dimethyl-p-aminoethylstyrene, N,N-diethyl-p-amino-ethylstyrene and vinylpyridine. Of them, styrene and α -methylstyrene are particularly preferable.

[0014] The conjugated diene includes 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 2-methyl-1,3-pentadiene, 1,3-hexadiene, 4,5-diethyl-1,3-octadiene, 3-butyl-1,3-octadiene and chloroprene. In order to obtain a hydrogenated diene block copolymer of excellent properties and industrial utilization, 1,3-butadiene, isoprene and 1,3-pentadiene are preferable, and 1,3-butadiene is more preferable.

[0015] In the hydrogenated diene block copolymer of this invention selected from an (A)-(B) block copolymer consisting of Block (A) and Block (B), an (A)-(B)-(C) block copolymer consisting of Block (A), Block (B) and Tapered Block (C), and an (A)-(B)-(A) block copolymer consisting of Block (A), Block (B) and Block (A), the weight proportion of the alkenyl aromatic compound/the conjugated diene in the total monomers is required to be 5/95 to 60/40, preferably 7/93 to 40/60.

[0016] When the proportion of the alkenyl aromatic compound is less than 5% by weight, the resulting hydrogenated diene block copolymer, when blended with other resin, gives a resin composition with insufficient improvement. When the hydrogenated diene block copolymer is blended with, for example, a polypropylene, the resulting composition has insufficient balance in impact resistance and rigidity. When the proportion of the alkenyl aromatic compound is more than 60% by weight, the resulting hydrogenated diene block copolymer is resinous and, when blended with other resin, gives a resin composition with insufficient improvement in impact resistance, particularly low-temperature impact resistance.

[0017] The content of the bound alkenyl aromatic compound in at least one Block (A) is at least 3% by weight, preferably 3-20% by weight, more preferably 5-15% by weight, and the total of the bound alkenyl aromatic compound contents in two Blocks (A) or Block (A) and Tapered Block (C) is 3-50% by weight, preferably 5-40% by weight, more preferably 5-25% by weight. When the content of the bound alkenyl aromatic compound in at least one Block (A) or the total of the bound alkenyl aromatic compound contents in two Blocks (A) or Block (A) and Tapered Block (C) is less than 3% by weight based on the total monomers, the resulting hydrogenated diene block copolymer tends to cause blocking when pelletized and give poor appearance when blended with other resin. When the total of the bound alkenyl aromatic compound contents in two Blocks (A) or Block (A) and Tapered Block (C) is more than 50% by weight, the resulting hydrogenated diene block copolymer is resinous and, when blended with other resin, provides a resin composition with insufficient improvement in impact resistance, particularly low-temperature impact resistance.

[0018] In order for the hydrogenated diene block copolymer to be able to give improved flexibility to a resin to be blended therewith, the vinyl content in the conjugated diene portion in Block (B) is more than 60%, more preferably 70% or more, particularly preferably 80% or more.

[0019] The vinyl content used herein refers to the content of the conjugated diene monomer unit formed by polymerization through the double bond of 1,2- or 3,4-position.

[0020] In the hydrogenated diene block copolymer of this invention, it is further required that at least 80%, preferably 90% or more, more preferably 95-100% of the double bonds of the conjugated diene portions is saturated by the hydrogenation. When less than 80% of the double bonds is saturated, the resulting hydrogenated diene block copolymer is inferior in heat resistance, weather resistance and ozone resistance.

[0021] Furthermore, the hydrogenated diene block copolymer of this invention has a polystyrene-reduced number-average molecular weight of 50,000-600,000, preferably 80,000-500,000. When the polystyrene-reduced number-average molecular weight is outside the above range, no sufficient improvement is obtained when the resulting hydrogenated diene block copolymer is blended with other resin. When the molecular weight is less than 50,000, the resulting composition has reduced impact resistance. When the molecular weight is more than 600,000, the composition has reduced fluidity, processability and appearance.

[0022] The hydrogenated diene block copolymer of this invention has a melt flow rate as measured at 230°C under a load of 12.5 kg, of preferably at least 0.1 g/10 min, more preferably at least 0.5 g/10 min. When the melt flow rate is less than 0.1 g/10 min, the resulting hydrogenated diene block copolymer is difficult to pelletize.

[0023] From the surface gloss standpoint, the hydrogenated diene block copolymer of this invention has a melt flow rate as measured at 230°C under a load of 5 kg, of preferably 0.1 g/10 min or more, more preferably 1-100 g/10 min.

[0024] The hydrogenated diene block copolymer of this invention can be obtained by subjecting Block (A), Block (B) and, as necessary, Tapered Block (C) or another Block (A) to living anionic polymerization in an organic solvent using an organic alkali metal compound as an initiator to form a block copolymer and then hydrogenating the block copolymer.

[0025] The organic solvent is a hydrocarbon solvent such as pentane, hexane, heptane, octane, methylcyclopentane, cyclohexane, benzene or xylene.

[0026] The organic alkali metal compound as an initiator is preferably an organolithium compound.

[0027] The organolithium compound is an organomonolithium compound, an organodilithium compound or an organopolylithium compound. Specific examples of these include ethyllithium, n-propyllithium, isopropyllithium, n-butyllithium, sec-butyllithium, tert-butyllithium, hexamethylenedithiolithium, butadienyllithium and isoprenyllithium. The organolithium compound is used in an amount of ordinarily 0.001-1 part by weight, preferably 0.02-0.2 part by weight per 100 parts by weight of the monomers.

[0028] In the above living anionic polymerization, a Lewis base (e.g. ether, amine) can be used as an agent for controlling the micro structure, i.e. the vinyl content of conjugated diene portion. The ether specifically includes diethyl ether, tetrahydrofuran, propyl ether, butyl ether, higher ethers, and ether derivatives of polyethylene glycols, such as ethylene glycol dibutyl ether, diethylene glycol dimethyl ether, diethylene glycol dibutyl ether and triethylene glycol dimethyl ether. The amine includes tetramethylethylenediamine, pyridine, tributylamine, etc. The Lewis base is used together with the above-mentioned organic solvent.

[0029] The polymerization reaction is effected usually at -30°C to +150°C.

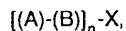
[0030] The living anionic polymerization can be effected by controlling the system temperature to a given temperature, or under a temperature increase without removing the heat generated.

[0031] The (A)-(B) block copolymer can be produced by any method. In general, however, first Block (A) or Block (B) is formed in the above-mentioned organic solvent in the presence of a polymerization initiator such as the above-mentioned alkali metal compound; then, Block (B) or Block (A) is formed. Either of Block (A) or Block (B) may be formed first.

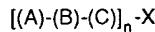
[0032] The boundary between Block (A) and Block (B) need not be made clear.

[0033] The (A)-(B)-(C) block copolymer or the (A)-(B)-(A) block copolymer can be produced by polymerizing an alkenyl aromatic compound in an organic solvent in the presence of an organolithium polymerization initiator to form Block (A), then polymerizing a conjugated diene and an alkenyl aromatic compound to form Block (B), and thereafter polymerizing a conjugated diene and an alkenyl aromatic compound to form Tapered Block (C) or polymerizing an alkenyl aromatic compound alone to form another Block (A). Alternatively, the above block copolymer can be produced by first forming Tapered Block (C) or Block (A), then forming Block (B) and further forming another Block (A).

[0034] The thus obtained (A)-(B) block copolymer, (A)-(B)-(C) block copolymer or (A)-(B)-(A) block copolymer may be reacted with a coupling agent and consequently may be changed to a longer chain or branched chain block copolymer as represented by the following general formula:

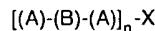


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or

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wherein (A), (B) and (C) are the same as defined above, n is an integer of 2-4 and X is a coupling agent residue.

[0035] The coupling agent includes, for example, diethyl adipate, divinylbenzene, tetrachlorosilicon, butyltrichlorosilicon, tetrachlorotin, butyltrichlorotin, dimethyldichlorosilicon, methylidichlorosilane, tetrachlorogermainium, 1,2-dibromoethane, 1,4-chloromethylbenzene, bis(trichlorosilyl)ethane, epoxidized linseed oil, tolylene diisocyanate and 1,2,4-benzenetriisocyanate.

[0036] The alkenyl aromatic compound content in the block copolymer can be controlled by the amount of monomer (s) fed in each polymerization stage, and the vinyl content in the conjugated diene portion in the block copolymer can be controlled by the amount of the micro structure-controlling agent used. The polystyrene-reduced number-average molecular weight and melt flow rate of the block copolymer can be controlled by the amount of polymerization initiator (e.g. n-butyllithium) to be added.

[0037] The hydrogenated diene block copolymer of this invention can be produced by dissolving the above-obtained block copolymer in an inert solvent and hydrogenating the copolymer with hydrogen of 1-100 kg/cm² at 20-150°C in the presence of a hydrogenation catalyst.

5 [0038] The inert solvent used in the hydrogenation includes hydrocarbon solvents such as hexane, heptane, cyclohexane, benzene, toluene and ethylbenzene, as well as polar solvents such as methyl ethyl ketone, ethyl acetate, diethyl ether, and tetrahydrofuran.

10 [0039] The hydrogenation catalyst includes catalysts consisting of a noble metal (e.g. palladium, ruthenium, rhodium or platinum) supported on carbon, silica or diatomaceous earth; catalysts consisting of a complex of rhodium, ruthenium or platinum; catalysts consisting of (1) a salt of an organic carboxylic acid with nickel or cobalt and (2) an organoaluminum or an organolithium; hydrogenation catalysts consisting of (1) a bis(cyclopentadienyl) group-containing transition metal compound and (2) a reducing organometal compound such as organoaluminum, organolithium or organomagnesium.

15 [0040] The hydrogenated diene block copolymer of this invention can also be produced by effecting a hydrogenation reaction using a reducing compound (e.g. lithium aluminum hydride or p-toluenesulfonyl hydrazide or a hydrogen storage alloy (e.g. Zr-Ti-Fe-V-Cr alloy, Zr-Ti-Nb-Fe-V-Cr alloy or LaNi₅ alloy).

[0041] The hydrogenation degree of the double bonds of the conjugated diene portion in Block (B) of the hydrogenated diene block copolymer of this invention can be controlled by changing the kind of the hydrogenation catalyst, the amount of reducing compound added, the hydrogen pressure in hydrogenation reaction and the reaction time.

20 [0042] The catalyst residue is removed from the solution containing the hydrogenated diene block copolymer; a phenol type or amine type antioxidant is added; and from the resulting copolymer solution can be easily isolated the hydrogenated diene block copolymer.

[0043] The isolation of the hydrogenated diene block copolymer can be effected, for example, by adding acetone or an alcohol to the copolymer solution to precipitate the copolymer, or by pouring the copolymer solution into boiling water with stirring to remove the solvent by vaporization.

25 [0044] The modified hydrogenated diene block copolymer of this invention can be obtained by introducing a functional group into the hydrogenated diene block copolymer.

[0045] The unsaturated compound used for introducing a functional group into the hydrogenated diene block copolymer is an unsaturated compound having at least one functional group selected from the group consisting of acid anhydride group, carboxyl group, hydroxyl group, amino group and epoxy group.

30 [0046] Specific examples of the unsaturated compound having an acid anhydride group or a carboxyl group are α, β-unsaturated carboxylic acids and their anhydrides such as acrylic acid, methacrylic acid, ethacrylic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid, itaconic anhydride, Hymic acid (trade name) and Hymic acid anhydride.

[0047] The unsaturated compound having a hydroxyl group includes hydroxypropyl (meth)acrylate and hydroxyethyl (meth)acrylate.

35 [0048] The unsaturated compound having an amino group includes diethylaminomethyl (meth)acrylate, dimethylaminoethyl (meth)acrylate and vinylpyridine.

[0049] The unsaturated compound having an epoxy group includes glycidyl (meth)acrylate, allyl glycidyl ether and vinyl glycidyl ether.

40 [0050] Of these, preferred are unsaturated compounds having an acid anhydride group or a carboxyl group, in view of the easy procedure of addition reaction to hydrogenated diene block copolymer. Particularly preferred are unsaturated compounds having an acid anhydride group.

[0051] The amount of unsaturated compound addition-bonded to the hydrogenated diene block copolymer is 0.01-20 parts by weight, preferably 0.2-5 parts by weight per 100 parts by weight of the hydrogenated diene block copolymer. When the amount is less than 0.01 part by weight, there can be obtained no sufficient improvement in impact resistance, chemical resistance and paintability (peeling resistance). When the amount is more than 20 parts by weight, there appears deterioration in electrical properties and moisture resistance.

[0052] The addition reaction of functional group-containing unsaturated compound to hydrogenated diene block copolymer of this invention can be effected utilizing the method described in Japanese Patent Publication No. 39-6384. That is, a hydrogenated diene block copolymer of this invention is used in place of an olefin rubber; the copolymer and a functional group-containing unsaturated compound are subjected to mixing-heating in a solid state, whereby addition reaction can be effected between them.

[0053] The mixing-heating can be effected batchwise using a closed type kneader, or continuously using an extruder. In this case, it is possible to add a peroxide to accelerate the reaction and, as necessary, to add a stabilizer.

55 [0054] To the (modified) hydrogenated diene block copolymer of this invention can be added conventional additives, for example, an antioxidant, a heat stabilizer, an ultraviolet absorber, a lubricant, a coloring agent and a flame retardant.

[0055] The (modified) hydrogenated diene block copolymer of this invention can be used as it is or as a modifier for various resins and is useful as a material for automobile parts, electric or electronic parts, films and sheets.

[0056] The (modified) hydrogenated diene block copolymer (I) of this invention can be used alone, or can be used

as a blend with a non-polar resin (II) and/or a polar resin (III) and, as necessary, other copolymer rubber.

[0057] The proportion of the resin to be blended with the (modified) hydrogenated diene block copolymer of this invention is 1-99% by weight, preferably 3-90% by weight. The optimum proportion is varied depending on the application purpose of the resulting blend.

5 [0058] The modification of resin by the (modified) hydrogenated diene block copolymer of this invention is unattainable when the copolymer is added in an amount of less than 1% by weight.

[0059] The non-polar resin (II) used in this invention includes polyethylene, high-molecular polyethylene, high-density polyethylene, medium-density polyethylene, low-density polyethylene, LLDPE (linear low-density polyethylene), polybutene, polyisobutylene, polypropylene, polystyrene, HIPS (high-impact polystyrene), polymethylstyrene and polymethylene. Preferable non-polar resins (II) are polypropylene, polyethylene and polystyrene.

10 [0060] The proportion of the present (modified) hydrogenated diene block copolymer/the non-polar resin (II) is 1-99% by weight/99-1% by weight. In order to obtain sufficient modification of the component (II) by addition of the component (I), the proportion of the component (I) is preferably 3-90% by weight, more preferably 5-70% by weight.

15 [0061] When the proportion of the component (I) is too low, no sufficient modification is obtained. When the proportion is too high, the inherent properties of the component (II) are sacrificed.

[0062] The (modified) hydrogenated diene block copolymer to be blended with the non-polar resin (II) is preferably the unmodified hydrogenated diene block copolymer. This unmodified hydrogenated diene block copolymer has good compatibility with the non-polar resin (II), and can give a composition with the non-polar resin (II) which is better balanced in impact resistance, processability, appearance, printability and paintability (peeling resistance), than an ethylene-propylene-(polyene) rubber which is conventionally used as a modifier.

20 [0063] In modifying a polypropylene resin widely used as, for example, a material for automobile bumper and instrumental panels, the proportion of the component (I)/the component (II) is 15-60/85-40 by weight in many cases. In this case, the rigidity-impact resistance balance of the composition is considerably higher than when a conventional ethylene-propylene rubber is used as a modifier.

25 [0064] When the component (I)-component (II) composition is formed into a film or a sheet, the weight proportion of the component (I)/the component (II) is 3-50/97-50 in many cases. In this case, the composition is superior in heat-seal strength and impact resistance.

30 [0065] The component (I)-component (II) composition is also suitable in the field of thermoplastic elastomers used as a material for automobile interior parts, bumper, etc. which are conventionally obtained by subjecting a polypropylene resin and an ethylene-propylene-polyene rubber as major components to partial crosslinking with a peroxide.

[0066] In this case, the component (I) and the component (II) are used in a weight proportion of 10/90 to 90/10, and for satisfying the requirements of fluidity and hardness, there are further added a mineral oil, a low-molecular polymer and a peroxide-decomposable polymer. This composition is superior to conventional compositions using, as a modifier, an ethylene-propylene-polyene rubber, in fluidity, mechanical strengths and appearance of molded article.

35 [0067] When in the composition of the hydrogenated diene block copolymer (I) and the non-polar resin (II), part or the whole of the component (I) is replaced by the modified hydrogenated diene block copolymer, the resulting composition has a slightly lower mechanical strength but higher paintability (peeling resistance) and chemical resistance.

[0068] When at least one (modified) hydrogenated diene block copolymer obtained from a diene block copolymer before hydrogenation represented by the general formula $[(A)-(B)-(C)]_n-X$, $[(A)-(B)]_n-X$ or $[(A)-(B)-(A)]_n-X$ [(A), (B) and (C) are the same as defined above, n is an integer of 2-4, and X is a coupling agent residue] is blended in a proportion of 40-90% by weight, preferably 50-80% by weight, more preferably 60-80% by weight, more preferably 60-80% by weight with 10-60% by weight, preferably 20-50% by weight, more preferably 20-40% by weight, of a polyolefin polymer, the resulting composition is a thermoplastic elastomer well balanced in mechanical properties, thermal ageing resistance, hardness (low hardness), elongation set (low tension set) and transparency.

40 [0069] When in the above case the proportion of the polyolefin polymer is more than 60% by weight, no composition can be obtained which is excellent in elongation set, hardness (low hardness) and thermoplastic elastomer properties. When the proportion is less than 10% by weight, no composition can be obtained which is excellent in mechanical properties and thermal ageing resistance.

45 [0070] In obtaining a thermoplastic elastomer composition, it is preferable to subject the (modified) hydrogenated diene block copolymer component to crosslinking according to a known crosslinking method. In the crosslinking method, there can be used peroxide crosslinking, resin crosslinking and sulfur crosslinking which are employed for ordinary rubbers. Peroxide crosslinking and resin crosslinking are preferable, and peroxide crosslinking is more preferable.

50 [0071] The specific crosslinking agent includes those crosslinking agents, crosslinking aids and crosslinking accelerators which are described in, for example, "Crosslinking Agents Handbook (by Shinzo Yamashita and Tosuke Kaneko, published by Taiseisha)".

[0072] The thermoplastic elastomer composition of this invention can contain an oil or a plasticizer as a softening agent in a proportion of 1-200 parts by weight per 100 parts by weight of the composition.

[0073] As the oil, there can be used an aromatic, naphthenic or paraffinic oil.

[0074] As the plasticizer, there can be used a phthalate, adipate, phosphate, polyether or polyester plasticizer.

[0075] In the composition of this invention comprising the (modified) hydrogenated diene block copolymer (I) and the non-polar resin (II), the non-polar resin (II) may be a combination of at least two non-polar resins and the composition may further comprise conventionally used compounding agents such as high polymer (e.g. ethylene-propylene-(polyene) rubber, hydrogenated styrene-butadiene-styrene triblock copolymer, hydrogenated acrylonitrile-butadiene copolymer, ethylenevinyl acetate copolymer, butyl rubber or the like), reinforcing agent (e.g. inorganic whiskers or carbon black), softening agent (e.g. mineral oil or low-molecular weight polymer), anti-oxidant, light stabilizer and slip agent.

[0076] The method of producing the above composition is not critical and can be a conventional method. In producing, for example, a composition comprising the (modified) hydrogenated diene block copolymer (I) and a polypropylene resin (II), there can be used, for example, a method wherein the two components are treated by a kneading means such as extruder, kneader, blender, Banbury mixer and roll, a method wherein a polypropylene is produced in the presence of the (modified) hydrogenated diene block copolymer of this invention to obtain the composition of this invention, or a method which is a combination of the above two methods.

[0077] By melt-mixing (M) 10-90 parts by weight of an olefin resin and (N) 90-10 parts by weight of at least one of the (modified) hydrogenated diene block copolymers of this invention in the presence of a crosslinking agent, there can be obtained a polyolefin type thermoplastic elastomer composition suitable for low-hardness applications and superior in fatigue resistance, mechanical properties, moldability and appearance of molded article.

[0078] The olefin resin (M) is a crystalline olefin polymer obtained by subjecting α -olefin monomers such as ethylene, propylene and 1-butene to homopolymerization or copolymerization, and is preferably a crystalline polypropylene. In carrying out this invention, these olefin resins can be used alone or in combination of two or more.

[0079] In the above thermoplastic elastomer composition, the amount of the olefin resin (M) is 10-90% by weight, preferably 30-70% by weight.

[0080] When the amount of the olefin resin (M) is more than 10% by weight, the resulting composition is superior in strength and fatigue resistance. When the amount is not more than 90% by weight, the composition has excellent characteristics as elastomer in respect of hardness.

[0081] The above composition may further comprise, in order to additionally impart thereto a function possessed by conventional rubbers, a synthetic rubber (e.g. ethylene-propylene copolymer rubber, styrene-butadiene copolymer rubber, polyisoprene rubber, acrylic rubber, acrylonitrile-butadiene copolymer rubber, silicone rubber, hydrogenated acrylonitrile-butadiene copolymer rubber) or natural rubber.

[0082] As the crosslinking agent used in the above composition, there is ordinarily used a radical-generating agent such as organic peroxide.

[0083] The organic peroxide includes 2,5-dimethyl-2,5-di(tert-butylperoxy)hexyne-3, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, 2,2'-bis(tert-butylperoxy)-p-diisopropylbenzene, dicumyl peroxide, di-tert-butyl peroxide, tert-butyl peroxybenzoate, 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane, 2,4-dichlorobenzoyl peroxide, benzoyl peroxide and p-chlorobenzoyl peroxide. Preferably, an organic peroxide of higher decomposition temperature is selected and used. In adding the organic peroxide, it is preferable to add a monoolefin copolymer rubber of an organic peroxide to a master batch.

[0084] The amount of the organic peroxide added is 0.3-1.5 parts by weight, preferably 0.5-1.0 part by weight per 100 parts by weight of the component (N).

[0085] When the amount of the organic peroxide added is more than 0.3 part by weight, the component (N) has a high crosslinking density and the resulting composition has excellent mechanical strengths. When the addition amount is more than 1.5 parts by weight, the component (N) has too high a crosslinking density and the composition has a reduced elongation.

[0086] In the crosslinking of the component (N), it is possible to use, as a co-crosslinking agent, an alkenyl compound monomer of bifunctionality or higher functionality. Such a co-crosslinking agent includes the following compounds: ethylene dimethacrylate, 1,3-butylene dimethacrylate, 1,4-butylene dimethacrylate, 1,6-hexanediol dimethacrylate, polyethylene glycol dimethacrylate, 1,4-butanediol diacrylate, 1,6-hexanediol diacrylate, 2,2'-bis(4-methacryloyldioxyphenyl)propane, trimethylolpropane trimethacrylate, trimethylolpropane triacrylate, pentaerythritol triacrylate, divinylbenzene, N,N'-methylenebisacrylamide, p-quinone dioxime, p,p'-dibenzoylquinone dioxime, m-phenylenebismaleimide and 4,4'-diphenylmethanebismaleimide.

[0087] The thermoplastic elastomer composition of this invention can comprise auxiliary additives conventionally used in rubbers and resins. Such auxiliary additives are the following commercially available ones: softening agents and plasticizers used for rubbers; fillers such as carbon black, white carbon, clay, talc, calcium carbonate and the like; antioxidant; heat stabilizer; ultraviolet absorber; coloring agent; processing aid and lubricant.

[0088] Production of the composition of this invention can be effected by melt-mixing given amounts of an olefin resin (M) and a hydrogenated diene block copolymer (N) by means of a preheated roll mill, a closed type kneader (e.g. Banbury mixer, pressure type kneader) or an extruder and simultaneously allowing a crosslinking agent to act. In a preferable production method, an olefin resin (M) and a hydrogenated diene block copolymer (N) are melt-mixed in a

kneader; when the melt-kneading has been completed, a crosslinking agent is added; then, the components (M) and (N) are reacted while dispersing the crosslinking agent.

[0089] Alternatively, the hydrogenated diene block copolymer (N) is partially crosslinked in the presence of a part of the olefin resin (M), then the remainder of the olefin resin (M) is added, and kneading is conducted.

[0090] The polar resin (III) used in this invention, when it is a thermoplastic resin, includes ABS resin; acrylic resin; polyacrylamide; polyacrylic acid; polyalkyl acrylates such as polymethyl acrylate, polyethyl acrylate and the like; polyacrylonitrile; acrylonitrile-styrene copolymer; polymethacrylamide; polymethacrylic acid; polyalkyl methacrylates such as polymethyl methacrylate, polyethyl methacrylate and the like; polymethacrylonitrile; acetal resin; polyoxymethylene; ionomer; chlorinated polyethylene; coumarone-indene resin; regenerated cellulose; petroleum resins; cellulose derivatives; alkali celluloses; cellulose esters; cellulose acetate; cellulose acetate butyrate; cellulose xanthate; cellulose nitrate; cellulose ethers; carboxymethyl cellulose; cellulose ether esters; fluoroplastics; FEP; polychlorotrifluoroethylene; polytetrafluoroethylene; polyvinylidene fluoride; polyvinyl fluoride; aliphatic polyamides such as nylon 6,10, nylon 6,12, nylon 6,6 and nylon 4,6; aromatic polyamides such as polyphenyleneisophthalamide, polyphenyleneterephthalamide, polymetaxyleneamide and the like; polyimides; polyphenylene sulfide; polyether-etherketones; polyamide-imides; polyarylates; polyethylene terephthalate; polyvinylidene chloride; polyvinyl chloride; chlorinated polyethylene; chlorosulfonated polyethylene; polycarbonates; polysulfone; polyethersulfones; polysulfonamide; polyvinyl alcohol; polyvinyl esters; polyvinyl cinammate; polyvinyl acetate; polyvinyl ether; polyisobutyl vinyl ether; polymethyl vinyl ether; polyphenylene oxide and polybutylene terephthalate. The polar resin (III), when it is a thermosetting resin, includes amino resin, aniline resin, urea resin, polysulfonamide, melamine resin, allyl resin, diallyl phthalate resin, alkyd resin, epoxy resin, silicone resin, vinyl ester resin, phenolic resin, novolac resin, resorcinol resin, unsaturated polyester resin, low-shrinkage unsaturated polyester and furan resin. Of these polar resins (III), preferable are polyamide, polyacetal, polyethylene terephthalate, polybutylene terephthalate, polycarbonate, polysulfone, polyphenylene oxide, epoxy resin and phenolic resin.

[0091] The proportion of the modified hydrogenated diene block copolymer (I) of this invention/the polar resin (III) is 1-99% by weight/99-1% by weight. In order for the component (III) to be sufficiently modified by the addition of the component (I), the proportion of the component (I) is preferably 3-60% by weight, more preferably 5-50% by weight. When the proportion of the component (I) is too low, no sufficient modification is obtained and, when the proportion is too high, the inherent properties of the component (III) are sacrificed.

[0092] The composition of the (modified) hydrogenated diene block copolymer (I) and the thermoplastic polar resin (III) described first. The (modified) hydrogenated diene block copolymer (I) of this invention, when added to the thermoplastic polar resin (III), gives a composition wherein the mechanical strengths and impact resistance of the resin (III) are well improved and which has excellent appearance of molded article.

[0093] The above composition of this invention shows a higher modification effect than compositions using, as a modifier for thermoplastic polar resin (III), conventional styrene-butadiene random copolymer, styrene-butadiene block copolymer or polybutadiene.

[0094] Blending the (modified) hydrogenated diene block copolymer (I) of this invention into, for example, a thermoplastic polyester gives an improvement in peeling resistance, to the polyester. Blending the copolymer (I) into a polyamide gives low reduction in heat resistance. Blending into a polyphenylene sulfide gives a composition of good processability.

[0095] Production of a composition of an unmodified hydrogenated diene block copolymer (I) and a thermoplastic polar resin (III) is preferably effected by compatibilization of the two components using, if necessary, a compatibilizing agent, in view of the impact resistance of the composition and its appearance of molded article. However, in producing a composition of a modified hydrogenated diene block copolymer and a thermoplastic polar resin (III), the above compatibilization is unnecessary because the former shows good compatibility with the latter.

[0096] The method of compatibilization includes a method wherein at the time of kneading an unmodified hydrogenated diene block copolymer (I) and a polar resin (III), there are added an unsaturated compound having at least one functional group selected from the group consisting of acid anhydride group, carboxyl group, hydroxyl group, amino group, epoxy group, oxazolyl group and imido group and, as necessary, a peroxide; a method wherein the above-mentioned functional group-containing unsaturated compound and a peroxide are added to a hydrogenated diene block copolymer (I), they are heat-treated to graft the unsaturated compound onto the hydrogenated diene block copolymer, the resulting graft copolymer is blended with a thermoplastic polar resin (III); and a method wherein other polymer having the above-mentioned functional group is used as a compatibilizing agent.

[0097] Said unsaturated compounds having at least one functional group include unsaturated acid anhydrides such as maleic anhydride, itaconic anhydride and the like; unsaturated acids such as acrylic acid and methacrylic acid; epoxy group-containing unsaturated compounds such as glycidyl methacrylate and allyl glycidyl ether; amino group-containing unsaturated compounds and their substitution derivatives such as p-aminostyrene, acrylamide and the like; hydroxyl group-containing unsaturated compounds such as hydroxyethyl acrylate; maleimide compounds such as cyclohexylmaleimide and phenylmaleimide; oxazolyl group-containing unsaturated compounds such as vinyloxazoline.

[0098] The said other polymer having particular functional group is a random, block or graft copolymer of the above-mentioned functional group-containing unsaturated compound and other vinyl monomer copolymerizable therewith.

[0099] Specific examples of the said other copolymer having a particular functional group include copolymers of styrene, the above-mentioned functional group-containing unsaturated compound and, as necessary, at least one other vinyl monomer copolymerizable with them, such as styrene-glycidyl methacrylate copolymer, styrene-maleic anhydride copolymer, styrene-methacrylic acid copolymer and styrene-acrylonitrile-methacrylic acid copolymer. Other examples of the said other copolymer having a particular functional group include copolymers of ethylene, the functional group-containing unsaturated compound and, as necessary, at least one other vinyl monomer copolymerizable with them, such as ethylene-glycidyl methacrylate copolymer and ethylene-glycidyl methacrylate-vinyl acetate copolymer, as well as graft copolymers obtained by grafting such an ethylene copolymer with other polymer. The said other polymer used for grafting include polymers obtained by polymerizing radical-polymerizable vinyl monomers, such as polyalkyl (meth) acrylate, polystyrene, styrene-acrylonitrile copolymer and styrene-alkyl (meth)acrylate copolymer, as well as polymers obtained by copolymerizing the above monomers with the functional group-containing unsaturated compound.

[0100] The copolymer as a compatibilizing agent further includes copolymers of butadiene, the functional group-containing unsaturated compound and, as necessary, other vinyl monomer copolymerizable with them, their hydrogenation products, and graft copolymers obtained by grafting said butadiene copolymer with other polymer as mentioned above.

[0101] When also in the production of a composition of a modified hydrogenated diene block copolymer (I) and a thermoplastic polar resin (III) there is used the above-mentioned compatibilization method, i.e. the method wherein an unsaturated compound having a particular functional group and, as necessary, a peroxide are added at the time of kneading, or the method wherein a compatibilizing agent is added, the resulting composition has further improved compatibility and properties.

[0102] The amount of the compatibilizing agent used is preferably 0.01-400 parts by weight, more preferably 0.1-100 parts by weight per 100 parts by weight of a total of the resin and the hydrogenated diene block copolymer. When the amount is less than 0.01 part by weight, no sufficient compatibilization effect can be obtained. When the amount is more than 400 parts by weight, the resulting composition has reduced properties.

[0103] To the composition of the (modified) hydrogenated diene block copolymer (I) of this invention and the thermoplastic polar resin (III) can be added, besides the compatibilizing agent, other rubbery polymer. The rubbery polymer includes polybutadiene, acrylonitrile-butadiene copolymer, its hydrogenation product, ethylene- α -olefin copolymer, ethylene- α -olefin-polyene copolymer, polyacrylic acid ester, styrene-butadiene block copolymer, hydrogenated styrene-butadiene block copolymer, ethylene-propylene elastomer grafted with styrene and ethylenic ionomer. These rubbery polymers can be used alone or in admixture of two or more.

[0104] The styrene-butadiene block copolymer includes ABA type, ABA tapered type and radial tereblock type.

[0105] The composition of the modified hydrogenated diene block copolymer (I) of this invention and the thermoplastic polar resin (III) can be obtained by kneading the two components preferably at a temperature of 200-350°C using an extruder, a Banbury mixer, a kneader or rolls.

[0106] The kneading can be effected in one stage, or in multi-stage in which either of the components is kneaded first and then the remainder of the components is added thereto and kneaded therewith.

[0107] In kneading, preferably, a continuous kneader and an extruder are used in combination, or an extruder alone is used. As the extruder, a screw unidirectionally rotating extruder is particularly preferable.

[0108] To the thermoplastic resin composition comprising the (modified) hydrogenated diene block copolymer (I) of this invention and the thermoplastic polar resin (II) can be added, alone or in combination of two or more, known fillers such as glass fiber, carbon fiber, metal fiber, glass beads, asbestos, mica, calcium carbonate, potassium titanate whiskers, talc, aramid fiber, barium sulfate, glass flakes and fluoroplastic.

[0109] The glass fiber and the carbon fiber preferably have a fiber diameter of 6-60 μm and a fiber length of 30 μm or more.

[0110] These fillers are added in an amount of preferably 5-150 parts by weight per 100 parts by weight of the thermoplastic resin composition, in order to obtain the addition effect.

[0111] To the thermoplastic resin composition can further be added other known additives such as antioxidant, plasticizer, coloring agent and lubricant. Furthermore, other known polymers can be added depending upon the properties required for the composition.

[0112] The thermoplastic resin composition of this invention comprising the component (I) and the component (III) can be formed into various molded articles by injection molding, sheet extrusion, vacuum molding, profile molding and foam molding.

[0113] The molded articles obtained by the above molding methods can be used as a material for automobile exterior or interior parts, electric or electronic parts and housings for their excellent properties.

[0114] The thermoplastic resin composition comprising (a) 1-90% by weight of at least one of the (modified) hydrogenated diene block copolymers of this invention (b) 5-94% by weight of a thermoplastic polyester and/or a thermo-

plastic polyester elastomer [hereinafter referred to as "component (b)"] and (c) 5-94% by weight of other thermoplastic polymer [hereinafter referred to as "component (c)"], is a thermoplastic resin composition having excellent impact resistance and giving molded articles of excellent appearance and properties.

[0115] The amount of the component (a) used in the above thermoplastic resin composition is 1-90% by weight, preferably 1-80% by weight, more preferably 5-80% by weight, particularly preferably 5-70% by weight. When the amount is less than 1% by weight, the resulting composition has no improvement in impact resistance. When the amount is more than 90% by weight, the composition has poor impact resistance and appearance of molded article.

[0116] The thermoplastic polyester used in the component (b) includes, for example, fully aromatic polyesters obtained by condensation polymerization of (1) an aromatic dicarboxylic acid or its derivative and (2) an aromatic diol or its derivative, and aromatic polyesters obtained by condensation polymerization of (1) an aromatic dicarboxylic acid or its derivative and (2) an aliphatic diol. The aromatic polyesters are preferable.

[0117] Preferably, the aromatic polyesters are polymers or copolymers obtained by condensation of terephthalic acid and an alkylene glycol. Particularly preferably, the aromatic polyesters are polybutylene terephthalate and polyethylene terephthalate, and their molecular weights are preferably such that the intrinsic viscosities as measured at 30°C using o-chlorophenol as a solvent are 0.2-2.0 dL/g.

[0118] The thermoplastic polyester elastomer in the component (b) has a high-melting crystalline segment (X) consisting of an aromatic polyester unit and a low-melting polymer segment (Y) consisting mainly of an aliphatic polyether or aliphatic polyester unit.

[0119] The weight ratio of (X)/(Y) in the thermoplastic polyester elastomer is 10-95/90-5.

[0120] The high-melting crystalline segment (X) consists of at least one dicarboxylic acid having a molecular weight of less than 300 and at least one alkylene glycol or cycloalkylene glycol having a molecular weight of less than 300.

[0121] The low-melting polymer segment (Y) consists of at least one long-chain glycol alone having a molecular weight of 400-6,000, or of at least one said long-chain glycol and at least one dicarboxylic acid having a molecular weight of less than 300.

[0122] The component (b) can be replaced by (b') a thermoplastic polyamide and/or a thermoplastic polyamide elastomer.

[0123] The thermoplastic polyamide is, for example, a polyamide ordinarily obtained by condensation of (1) a linear diamine represented by $H_2N-(CH_2)_x-NH_2$ (x is an integer of 4-12) and (2) a linear dicarboxylic acid represented by $HOOC-(CH_2)_y-COOH$ (y is an integer of 2-12) and a polyamide obtained by ring-opening polymerization of lactam.

[0124] Preferable examples of these polyamides are nylon 6,6, nylon 6,9, nylon 6,10, nylon 6,12, nylon 6, nylon 12, nylon 11 and nylon 4,6.

[0125] There can also be used copolymeric polyamides such as nylon 6/6,6, nylon 6/6,10, nylon 6/12, nylon 6/6,12, nylon 6/6,6/6,10, nylon 6/6 and 6/12.

[0126] The polyamide elastomer used as the component (b') can be an elastomer synthesized by a condensation reaction between a polyamide and a polyether having a hydroxyl group at the chain terminal.

[0127] The polyether having a hydroxyl group at the chain terminal can be a straight chain or branched chain polyoxalkylene glycol [e.g. polyoxyethylene glycol, polyoxypropylene glycol, polyoxetramethylene glycol], their mixture, or a copolyether derived from the polyoxalkylene glycol. The average molecular weight of the polyether is generally 200-6,000, preferably 400-3,000.

[0128] The amount of the polyoxalkylene glycol in the total components is usually 5-85% by weight, preferably 10-50% by weight.

[0129] The polyamide includes a lactam whose hydrocarbon chain has 4-14 carbon atoms and an amino acid condensation product.

[0130] (b") A polyphenylene ether can be used in place of the component (b).

[0131] Specific examples of the polyphenylene ether are particularly preferably a polymer obtained from 2,6-dimethylphenol, and a copolymer obtained from 2,6-dimethylphenol and 2,3,6-trimethylphenol.

[0132] The intrinsic viscosity [η] of the polyphenylene ether (b") as measured at 30°C in chloroform is not critical but is preferably 0.2 dL/g, more preferably 0.25-0.7 dL/g.

[0133] The amount of the component (c) used is preferably 5-94% by weight, more preferably 10-90% by weight based on the total amount of the components (a) to (c). When the amount is 5% by weight or more, the resulting composition has excellent heat resistance, but when the amount is more than 94% by weight, the resulting composition is inferior in impact resistance, surface appearance of molded article and moldability.

[0134] In the above composition, the total amount of the components (b) and (c) used is 99-10% by weight, preferably 99-20% by weight, more preferably 95-30% by weight. When the total amount is more than 99% by weight, the resulting composition is inferior in impact resistance. By making the total amount 10% by weight or more, there can be obtained a composition having excellent impact resistance and surface appearance of molded article.

[0135] The ratio of the component (b)/the component (c) is preferably 90-10% by weight/10-90% by weight, more preferably 80-20% by weight/20-80% by weight, particularly preferably 70-30% by weight/30-70% by weight.

5 [0136] To the above thermoplastic resin composition can be applied the same compatibilization method as mentioned above concerning the composition of the unmodified hydrogenated diene block copolymer (I) and the thermoplastic polar resin (III), for improving the compatibility.

[0137] For the purpose of improvement of compatibility and/or properties, there may be added to the composition at the time of its production, the same unsaturated compound having a functional groups as mentioned above in combination, as necessary, with an organic peroxide.

10 [0138] Preferable results are obtained in some cases when a crosslinking agent ordinarily used in rubbers is added to the above composition at the time of its production in order to crosslink the rubbery polymers used as the components (a) and (b).

15 [0139] The crosslinking agent can be an organic peroxide alone; its combination with a crosslinking aid such as bismaleimide crosslinking aid, dimethacrylic crosslinking aid, diallyl crosslinking aid, trimethacrylic crosslinking aid or oxime compound; sulfur alone; a sulfur-containing organic compound alone (e.g. tetramethylthiuram disulfide) or its combination with a vulcanization accelerator.

[0140] The above thermoplastic resin composition can be formed into various molded articles by injection molding, sheet molding, vacuum molding, profile molding, foam molding, blow molding and stampable molding.

20 [0141] The molded articles can be used as a material for automobile exterior or interior parts, electric or electronic parts and housings, for their excellent properties.

25 [0142] Next, a description is made on the composition comprising the (modified) hydrogenated diene block copolymer (I) of this invention and a thermosetting polar resin (III). The (modified) hydrogenated diene block copolymer (I) of this invention, when blended with a thermosetting polar resin (III), can give a composition retaining the excellent strength and impact resistance possessed by the resin (III) and further having excellent heat resistance and electrical insulation. This composition is highly improved as compared with conventionally used acrylonitrile-butadiene rubber and carboxyl group-containing acrylonitrile-butadiene rubber.

30 [0143] When in production of a composition of the (modified) hydrogenated diene block copolymer (I) and the thermosetting polar resin (III), there is used a modified hydrogenated diene block copolymer as the component (I), the resulting composition has excellent compatibility and exhibits the effects as intended by this invention, at a higher level. Therefore, a modified hydrogenated diene block copolymer is preferable as the component (I). The functional group-containing unsaturated compound used as a graft monomer (a modifying agent) in the production of the modified hydrogenated diene block copolymer, is preferably an acid anhydride group- or carboxyl group-containing unsaturated compound because it can be easily grafted. An acid anhydride group-containing compound is particularly preferable because this compound is widely used as a curing agent for thermosetting resins such as epoxy resin and, even if partially remains unreacted, it gives no adverse effect on thermosetting resins.

35 [0144] Mixing the (modified) hydrogenated diene block copolymer (I) with the thermosetting polar resin (III) has no restriction, and it can be effected using a closed type mixer (e.g. Banbury mixer), rolls or an extruder depending upon the mixing ratio of the component (I)/the component (III).

40 [0145] The composition of the (modified) hydrogenated diene block copolymer (I) of this invention and the thermosetting polar resin (III) can comprise, as necessary, an antioxidant, a stabilizer, a plasticizer, a softening agent, inorganic and organic fillers, a reinforcing agent and a crosslinking agent.

[0146] The composition comprising, as main components, the (modified) hydrogenated diene block copolymer (I) of this invention and the thermosetting polar resin (III) is widely used mainly in electronic parts, and also in coating material, casting material, molding material, adhesive and paint.

45 [0147] In the above description, the composition of the (modified) hydrogenated diene block copolymer (I) and a resin has been explained referring to the composition of the component (I) and the non-polar resin (II) and the composition of the component (I) and the polar resin (III). However, the composition of this invention includes also a composition of the component (I), the component (II) and the component (III).

[0148] This invention is described in more detail referring to Examples. However, this invention is not restricted to these Examples.

50 [0149] In the Examples, parts and % are by weight unless otherwise specified. Various properties as mentioned in the Examples were measured by the following methods.

[0150] Bound styrene content was measured by an infrared analysis, based on the phenyl group absorption at 679 cm⁻¹.

[0151] Vinyl content was calculated according to the Hampton method using an infrared analysis.

55 [0152] Hydrogenation degree was calculated from the ¹H-NMR spectrum obtained at 100 MHz using tetrachloroethylene as a solvent.

[0153] Molecular weight was obtained as a polystyrene-reduced molecular weight, by gel permeation chromatography at 135°C using trichlorobenzene as a solvent.

- [0154] Melt flow rate was measured at 230°C under a load of 12.5 kg, 5 kg or 2.16 kg in accordance with JIS K 7210.
 [0155] Blocking tendency of pellets was measured by preparing round pellets using a 55-mmΦ single-screw extruder and a hot cutter, placing them in a constant temperature bath of 40°C under a load of 30 g/cm² for 24 hours to allow them to stick to each other and form blocks, and rating the blocks as follows.

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- ◎: Blocks can be disintegrated very easily.
- : Blocks can be disintegrated relatively easily.
- ×: Blocks are difficult to disintegrate.

10 [0156] Izod impact strength was measured according to JIS K 7110, using an injection-molded article with notch.

- [0157] Izod impact strength after thermal ageing was measured by placing an injection-molded article with notch in a Geer oven set at 150°C, for 120 hours or 70 hours, then cooling the article to room temperature and subjecting the article to the above test according to JIS K 7110.

- [0158] Flexural modulus was measured in accordance with JIS K 7203.

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- [0159] Surface gloss was measured in accordance with JIS K 7105.

- [0160] Film peeling strength was measured by degreasing a 2-mm thick sheet obtained by injection molding, with ethanol, subjecting the sheet to a surface treatment by trichloroethane vapor, coating the resulting sheet first with a primer (RB291H manufactured by Nihon B Chemical K.K.) and then with a polyurethane type paint (R263 manufactured by the same company) so that the film thickness (as dried) of the paint became about 50 microns, and after the film has been cured, peeling the film at 180° at a drawing speed of 30 mm/min.

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- [0161] Amount of functional group-containing unsaturated compound (modifying monomer) added was measured by examining $\nu_{C=O}$ (stretching vibration of carboxyl group) using the calibration curve method by infrared absorption spectrum.

- [0162] Appearance of molded article was evaluated visually in accordance with the following rating standard.

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- : Appearance is good.
- ×: Has poor appearance as represented by iridescent luster, flow marks, surface roughening, etc.

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- [0163] Tensile strength (T_B) was obtained by measuring a breaking strength (kg·f/cm²) at a drawing speed of 500 m/min using a JIS No. 3 dumbbell.

- [0164] Tensile elongation (T_E) was obtained by measuring an elongation (%) up to breakage under the same test conditions as used for the above tensile strength.

- [0165] Thermal ageing resistance was obtained by allowing a JIS No. 3 dumbbell to stand in a Geer oven at 110°C for 168 hours and then subjecting the resulting dumbbell to measurement of tensile strength (T_B) and tensile elongation (T_E).

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- [0166] Hardness was measured as a JIS hardness.

- [0167] Tension set was obtained by stretching a JIS No. 3 dumbbell by 100%, maintaining the condition for 10 minutes, then measuring the length after 10 minutes, and calculating the tension set. A larger tension set indicates that the product is inferior in properties as thermoplastic elastomer.

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- [0168] Transparency was obtained by visually evaluating the transparency of a molded article (JIS No. 3 dumbbell) according to the following rating standard.

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- : Good transparency.
- Δ: Translucent.
- ×: Opaque.

- [0169] Volume resistivity was measured in accordance with ASTM D 257-61.

Example 1 (Preparation of hydrogenated diene block copolymer Q-2)

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- [0170] Into a 10-liter autoclave were fed 5,000 g of degassed and dehydrated cyclohexane, 900 g of 1,3-butadiene and 60 g of styrene. Thereto were added 200 g of tetrahydrofuran and 0.3 g of n-butyllithium, and adiabatic polymerization was effected starting from 10°C. After 45 minutes, 40 g of styrene was added and further polymerization was effected.

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- [0171] The reaction mixture was controlled at 70°C and there were added 1.5 g of n-butyllithium and 1.5 g of 2,6-di-tert-butyl-p-cresol, followed by addition of 0.5 g of bis(cyclopentadienyl)titanium dichloride and 2 g of diethylaluminum chloride. The resulting mixture was hydrogenated at a hydrogen pressure of 10 kg/cm² for 1 hour.

- [0172] The reaction mixture was returned to an atmosphere of room temperature and atmospheric pressure, taken

out of the autoclave, and poured into water with stirring. The solvent was removed by steam distillation to obtain a hydrogenated polymer (hereinafter referred to as Copolymer Q-2).

[0173] The resulting hydrogenated polymer (hereinafter referred to as Copolymer Q-2) has a hydrogenation degree of 97%, a polystyrene-reduced number-average molecular weight of 310,000 and a melt flow rate of 2.3 g/10 min as measured at 230°C under a load of 12.5 kg.

[0174] The vinyl content of the butadiene portion of the polymer before hydrogenation was 80%.

Example 2 (Preparation of hydrogenated diene block copolymer Q-4)

[0175] Into a 10-liter autoclave were fed 5,000 g of degassed and dehydrated cyclohexane and 40 g of styrene. Thereto were added 200 g of tetrahydrofuran and 0.3 g of n-butyllithium. The resulting mixture was subjected to adiabatic polymerization for 30 minutes starting from 50°C. The reaction mixture was cooled to 10°C, and 600 g of 1,3-butadiene and 170 g of styrene were added. The resulting mixture was subjected to polymerization. 95 g of styrene and 95 g of 1,3-butadiene were further added, and the polymerization was continued. Then, the reaction mixture was subjected to the same hydrogenation reaction as in Example 1.

[0176] The resulting hydrogenated polymer (hereinafter referred to as Copolymer Q-4) had a hydrogenation degree of 98%, a polystyrene-reduced number-average molecular weight of 292,000 and a melt flow rate of 1.2 g/10 min as measured at 230°C under a load of 12.5 kg.

[0177] The vinyl content of the butadiene portion of the copolymer before hydrogenation was 78%.

Example 3 (Preparation of hydrogenated diene block copolymer Q-6)

[0178] Into a 10-liter autoclave were fed 5,000 g of degassed and dehydrated cyclohexane and 125 g of styrene. Thereto were added 200 g of tetrahydrofuran and 0.8 g of n-butyllithium. The mixture was subjected to adiabatic polymerization for 30 minutes starting from 50°C. The reaction mixture was cooled to 10°C. 700 g of 1,3-butadiene and 50 g of styrene were added and polymerization was effected. Further, 125 g of styrene was added and polymerization was effected. The reaction mixture was subjected to the same hydrogenation reaction as in Example 1.

[0179] The resulting hydrogenated copolymer (hereinafter referred to as Copolymer Q-6) had a hydrogenation degree of 97%, a polystyrene-reduced number-average molecular weight of 110,000 and a melt flow rate of 1.1 g/10 min as measured at 230°C under a load of 12.5 kg.

[0180] The vinyl content of the butadiene portion of the copolymer before hydrogenation was 77%.

[0181] In Table 1, there are shown the physical properties of the hydrogenated copolymers prepared in Examples 1 to 3. As is clear from Table 1, the hydrogenated diene block copolymers of this invention are pelletizable by themselves and accordingly have excellent processability.

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Table 1

		Example		
		1	2	3
Hydrogenated diene block copolymer	Copolymer Q-2		Copolymer Q-4	Copolymer Q-6
<u>Micro structure</u>				
① Total bound styrene content (%)	10	30.5	30	
② Proportion of total bound styrene content of Block (A) and Tapered Block (C) in total copolymer (%)	4.5	13.5	25	
③ Vinyl content of butadiene portion in Block (B) (%)	80	78	77	
<u>Properties of copolymer</u>				
① Hydrogenation degree (%)	97	99	97	
② Molecular weight ($\times 10^{-4}$)	31	29.2	11.0	
③ Melt flow rate (230°C, 12.5 Kg)	2.3	1.2	1.1	
④ Easiness of pelletization	○	○	○	
⑤ Blocking tendency of pellets	○	○	○	

Examples 4 and 5

(Preparation of compositions of hydrogenated diene block copolymer and non-polar resin)

- 5 [0182] 25 parts of one of the copolymers obtained in Examples 1-3 and 75 parts of a polypropylene resin (Polypropylene BC-2 manufactured by Mitsubishi Petrochemical Co., Ltd.) were melt-kneaded using a 4-liter Banbury mixer.
- [0183] Two kinds of the melt-kneaded products were pelletized and then subjected to injection molding to prepare test pieces for measurement of physical properties. The results of measurement of physical properties are shown in Table 2.
- 10 [0184] The compositions of Examples 4 and 5 are good in Izod impact strength, flexural modulus and surface gloss.

Table 2

Compounding recipe	Example	
	4	5
Copolymer (I) Type Parts	Copoly- mer Q-2 25	Copoly- mer Q-4 25
Non-polar resin (II) Type Parts	PP 75	PP 75
Physical properties		
Melt flow rate (230°C, 2.16 kg) (g/10 min)	13.0	12.0
Izod impact strength (kg·cm/cm)		
-20°C	12.0	14.5
-40°C	10.1	12.6
Flexural modulus (kg·f/cm ²)	2,500	2,400
Surface gloss (incident angle = 60°) (%)	45	50
Peeling strength of film (g/cm)	1.4	1.7

Examples 6 to 9 (Preparation of composition of hydrogenated diene block copolymer and thermosetting polar resin)

5 [0185] One of the hydrogenated diene block copolymers (Copolymer Q-2 and Q-4) obtained in Example 1 and 2 was grafted with maleic anhydride or glycidyl methacrylate to prepare a grafted product (a modified hydrogenated diene block copolymer), and the product was blended with a thermosetting polar resin to obtain a composition.

(1) Preparation of modified hydrogenated diene block copolymer - Examples 6 and 7.

10 [0186] 100 parts by weight of one of the hydrogenated diene block copolymers (Copolymer Q-2 or Q-4) obtained in Example 1 and 2 was maintained at 190°C and placed in a mixer (HAAKE RHEOCORD SYSTEM 40 RHEOMIX MIXER 600 manufactured by HAAKE BUCHLER CO.). After 2 minutes, 2.5 parts of maleic anhydride or glycidyl methacrylate was added and mixing was effected. Then, 0.15 part of an organic peroxide [2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, Perhexa 25B manufactured by NIPPON OIL & FATS CO., LTD.) was added, and kneading was continued for a further 5 minutes to obtain a hydrogenated diene block copolymer (hereinafter referred to as Copolymer Q-14 or Q-16).

15 [0187] The properties of Copolymers Q-14 and Q-16 are show in Table 3.

(2) Preparation of composition with thermosetting polar resin (epoxy resin composition)

- Examples 8 and 9

20 [0188] A thermosetting resin composition (an epoxy resin composition) was obtained according to the following procedure.

Compounding recipe	Parts
Copolymer Q-14 or Q-16	10
Cresol-novolac type epoxy resin (epoxy equivalent: 220)	100
Phenol resin (novolac type)	50
Curing agent (2-methylimidazole)	5

30 [0189] The above materials of the above amounts were kneaded using a closed type mixer at about 80°C. The kneaded product was press-molded at 160°C. The resulting plate was processed with a milling cutter to prepare test samples for measurement of physical properties.

35 [0190] In Comparative Examples 1-3, epoxy resin compositions were obtained in the same manner as in Examples 8 and 9, except that the modified hydrogenated diene block copolymer (Copolymer Q-14) was replaced by 10 parts of liquid carboxy NBR (Hycar CTBN manufactured by BF Goodrich Co.) (Comparative Example 1) or 10 parts of an acrylonitrile butadiene rubber (JSR N220S manufactured by Japan Synthetic Rubber Co., Ltd., bound acrylonitrile content = 41%, Mooney viscosity = 56) (Comparative Example 2) or was not used (Comparative Example 3). The epoxy resin compositions obtained in Examples 8 and 9 and Comparative Examples 1-3 were evaluated. The results of evaluation are show in Table 4.

40 [0191] As is clear from Table 4, the epoxy resin compositions of this invention have good mechanical strengths and superior heat resistance, flexibility and moldability.

Examples 10 and 11

45 [0192] A phenol resin composition was prepared according to the following procedure, using the modified hydrogenated diene block copolymer (Copolymer Q-14 or Q-16) obtained in the same manner as in Example 6.

Compounding recipe	Parts
Copolymer Q-14 or Q-16	10
Phenol resin (novolac type)	100
Curing agent (hexamethylenetetramine)	10

55 [0193] The above materials of the above amounts were kneaded at 130°C for 5 minutes using an electrically heated roll. The kneaded product was ground and press-molded at 160°C for 10 minutes to obtain a plate of 4 mm in thickness. The plate was processed in accordance with JIS K 6911 using a milling machine to prepare test pieces. The test pieces were measured for physical properties. The results of evaluation are shown in Table 5.

[0194] In Comparative Examples 4 and 5, compositions were obtained as in Examples 10 and 11, except that the modified hydrogenated diene block copolymer (Q-14 or Q-16) was replaced by CTBN or N220S as described in relation to Comparative Examples 1-3.

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Table 3

		Example	
		6	7
Modified hydrogenated diene block copolymer	Copolymer Q-14		
Compounding recipe (parts)			
Hydrogenated diene block copolymer	Copolymer Q-2		
Maleic anhydride	-		
Glycidyl methacrylate	2.5		
Perhexa 25B	-		
Analysis of grafted product (amount of monomer grafted, parts)	0.15		
Maleic anhydride	-		
Glycidyl methacrylate	0.39		
Modified hydrogenated diene block copolymer	99 or more		
Hydrogenation degree (%)	32		
Molecular weight ($\times 10^{-4}$)	30	○	
Easiness of pelletization	○	○	
Blocking tendency of pellets	○	○	○

Table 4

Compounding recipe	Example			Comparative Example			
		8	9	1	2	3	
Copolymer blended Type parts	Copolymer Q-14 10	Copolymer Q-16 10	CTBN	JSR N220S	-	-	
Physical properties							
Flexural modulus (kg.f/cm ²)	2.1	2.1	4.6	5.1	4.2		
Izod impact strength (23°C) (kg.cm/cm)	5.2	5.6	3.2	5.5	3.5		
Izod impact strength after thermal ageing*1 (23°C) (kg.cm/cm)	5.1	5.1	2.9	3.9	3.6		
Flow property (cc/sec, × 10 ⁻²)	3.5	3.2	3.4	3.0	6.3		

Note: *1: 150°C × 120 hours

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Table 5

		Example			Comparative Example		
		10	11	11	4	5	
<u>Compounding recipe</u>							
Copolymer blended							
Type							
parts							
<u>Physical properties</u>							
Flexural modulus (kg·f/cm ²)		1.8		1.9		2.2	2.2
Izod impact strength (23°C) (kg·cm/cm)		2.5		2.9		1.2	1.2
Izod impact strength after thermal ageing*1 (23°C) (kg·cm/cm)		2.2		2.3		1.0	1.0

Note: *1: 150°C × 120 hours

Examples 12 and 13

(Preparation of compositions of hydrogenated diene copolymer and polar resin)

5 [0195] One of the modified hydrogenated diene block copolymers and one of the polar resins all shown in Table 6 were melt-kneaded using a twin-screw extruder. The kneaded product (composition) was pelletized, dried thoroughly and subjected to injection molding to prepare test pieces for measurement of physical properties. The results of measurement of physical properties are shown in Table 6.

[0196] The compositions of Examples 12 & 13 are good in both impact resistance and appearance of molded article.

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Table 6

		Example	Example	Example
		12	13	13
<u>Compounding recipe</u>				
Copolymer (I)				
Type		Copolymer Q-14	Copolymer Q-16	Copolymer Q-16
Parts		20	20	20
Polar resin (III)				
Type		PBT*2	PC*4	PC*4
Parts		80	80	80
<u>Physical properties</u>				
Izod Impact strength (23°C) (kg.cm/cm)		NB	NB	NB
Appearance of molded article		O	O	O

Note:

*2: Polybutylene terephthalate (Duranex XD 499 manufactured by Polyplastic K.K.)

*4: Polycarbonate (Lupilon S-100 manufactured by MITSUBISHI GAS CHEMICAL CO., LTD.)

Examples 14 - 16

[0197] There were used, as component (M), a crystalline polypropylene (Mitsubishi Noblen MH-8 manufactured by Mitsubishi Petrochemical Co., Ltd.) and, as component (N), a hydrogenated random SBR having a styrene block at both terminals (styrene content = 15% in terminal blocks, 50% in random SBR; butadiene content = 35%; vinyl content = 80%; polystyrene-reduced number-average molecular weight = 300,000). The components (M) and (N) were kneaded according to the compounding recipes shown below and in Table 7 to prepare three crosslinked products. They were evaluated. The results are shown in Table 7.

[0198] The master batch of organic peroxide used in the above compounding was prepared by incorporating 10 parts of 2,5-dimethyl-2,5-di(tert-butylperoxy)hexyne-3 into 100 parts of an EPM ($ML_{1+4}^{100^{\circ}\text{C}} = 40$, propylene content = 49%) using a 6-inch roll.

Compounding recipe

[0199] The polyolefin resin and hydrogenated diene block copolymer shown in Table 7 were placed in a 1-liter pressure type kneader (a product of Moriyama Seisakusho) heated at 170°C, and kneaded until the polyolefin resin was melted. After the polyolefin resin and the hydrogenated diene block copolymer were melt-kneaded uniformly, a given amount of a master batch of organic peroxide was added, and kneading was continued for a further 10 minutes to allow the organic peroxide to act to obtain three thermoplastic elastomer compositions. Each of the compositions was formed into a sheet using a 12.54 cm (6-inch) roll; the sheet was made into cubic pellets using a cubing pelletizer; the pellets were processed by an injection machine to prepare plate-shaped test pieces for measurement of physical properties. The results of measurement are shown in Table 7.

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Table 7

Compound- ing recipe (part)	(M) Component Polyolefin resin PP	Example		
		14	15	16
(N)	Component Hydrogenated end-blocked random SBR	20	40	60
Crosslinking agent				
Peroxide master batch	80	60	40	
Co-crosslinking agent	2.0	2.0	2.0	
Divinylbenzene				
Extender oil (paraffinic oil)	0.20	0.30	0.24	
100% Tensile stress (kg/cm ²)	30	-	-	
300% Tensile stress (kg/cm ²)	22	74	126	
Tensile strength (kg/cm ²)	61	92	130	
Elongation at break (%)	65	133	175	
Hardness (Shore D)	350	550	500	
Fatigue resistance (Length of cracks which grow when flexed 10 ⁴ times)	60 (JIS A)	45	60	
Appearance of molded article	○	○	○	

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Example 17

[0200] The component (a) used in this Example was prepared as follows.

[Preparation of component (a) (synthesis of polymer R-1)].

R-1

5 [0201] Into a 10-liter autoclave were fed 5,000 g of degassed and dehydrated cyclohexane and 120 g of styrene (first stage). Thereto were added 200 g of tetrahydrofuran and 0.3 g of n-butyllithium, and adiabatic polymerization was effected for 30 minutes starting from 50°C.

[0202] The reaction mixture was cooled to 10°C. 704 g of butadiene and 176 g of styrene (second stage) were added, and polymerization was effected.

10 [0203] Then, the reaction mixture was adjusted to 70°C, and thereto were added 1.5 g of n-butyllithium, 1.5 g of 2,6-di-tert-butyl-p-cresol, 0.5 g of bis(cyclopentadienyl)titanium dichloride and 2 g of diethylaluminum chloride. Hydrogenation was effected at a hydrogen pressure of 10 kg/cm². The reaction mixture was returned to an atmosphere of room temperature and atmospheric pressure, taken out of the autoclave, poured into water, and subjected to steam distillation to remove the solvent, to obtain a hydrogenated diene block copolymer (hereinafter referred to Copolymer R-1).

[0204] The hydrogenated diene block copolymer (Copolymer R-1) had a hydrogenation degree of 98% and a polystyrene-reduced number-average molecular weight of 300,000. The 1,2-vinyl content of butadiene portion in the copolymer before hydrogenation was 80%.

20 [0205] The components shown in Table 8 were melt-kneaded in the proportions shown in Table 8 using a twin-screw extruder. The resulting composition was evaluated. In the composition was used, as a compatibilizing agent, 10 parts of an ethylene-glycidyl methacrylate copolymer-grafted styrene-acrylonitrile copolymer.

[0206] There were used, as the component (b), b-1 [polybutylene terephthalate] and, as the component (c), c-1 (ABS resin) and c-2 (polycarbonate).

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Table 8

	(a) Component	(b) Component	(c) Component	Evaluation results	
	Type and amount (parts)	Type and amount (parts)	Type and amount (parts)	Izod impact strength (kg.cm/cm)	Appearance of molded article
Example 17	R-1 10	b-1 40	c-2 40	76	○

Claims

1. A hydrogenated diene block copolymer having a polystyrene-reduced number-average molecular weight of 50,000-600,000 which is a hydrogenation product of an (A)-(B) block copolymer in which (A) means an alkenyl aromatic compound polymer block and (B) means an alkenyl aromatic compound-conjugated diene random copolymer block wherein the vinyl content of the conjugated diene portion is more than 60% an (A)-(B)-(C) block copolymer in which (A) and (B) are as defined above and (C) means an alkenyl aromatic compound-conjugated diene copolymer tapered block wherein the proportion of the alkenyl aromatic compound increases gradually, or an (A)-(B)-(A) block copolymer in which (A) and (B) are as defined above, in which block copolymer
- (1) the weight proportion of the alkenyl aromatic compound/the conjugated diene is 5/95 to 60/40, and
 (2) the content of the bound alkenyl aromatic compound in at least one block (A) is at least 3% by weight and the total of the bound alkenyl aromatic compound contents in the two blocks (A) or the block (A) and the block (C) is 3-50% by weight based on the total monomers,
- and in which hydrogenation product at least 80% of the double bond unsaturations of the conjugated diene portion is saturated by the hydrogenation.
2. The hydrogenated diene block copolymer according to Claim 1, wherein the block copolymer is a block copolymer represented by the general formula $[(A)-(B)]_n-X$, $[(A)-(B)-(C)]_n-X$ or $[(A)-(B)-(A)]_n-X$ wherein (A), (B) and (C) are the same as defined in Claim 1, n is an integer of 2-4 and X is a coupling agent residue.
3. A modified hydrogenated diene block copolymer obtainable by modifying 100 parts by weight of the hydrogenated diene block copolymer according to Claim 1 or 2 with 0.01-20 parts by weight of an unsaturated compound having at least one functional group selected from the group consisting of acid anhydride group, carboxyl group, hydroxyl group, amino group and epoxy group.
4. A hydrogenated diene block copolymer having a polystyrene-reduced number-average molecular weight of 100,000-600,000 which is a hydrogenation product of an (A)-(B) block copolymer consisting of (A) an alkenyl aromatic compound polymer block and (B) an alkenyl aromatic compound-conjugated diene random copolymer block, an (A)-(B)-(C) block copolymer consisting of the block (A), the block (B) and (C) an alkenyl aromatic compound-conjugated diene copolymer tapered block wherein the proportion of the alkenyl aromatic compound increases gradually, or an (A)-(B)-(A) block copolymer consisting of the block (A), the block (B) and the block (A), in which block copolymer
- (1) the weight proportion of the alkenyl aromatic compound/the conjugated diene is 5-40/95-60,
 (2) the total of the bound alkenyl aromatic compound contents in the block (A) and the block (C) or the two blocks (A) is 3-25% by weight based on the total monomers and the content of the bound alkenyl aromatic compound in at least one block (A) is at least 3% by weight, and
 (3) the vinyl content in the conjugated diene portion in the block (B) is more than 60%, and in which hydrogenation copolymer at least 90% of the double bonds of the conjugated diene portion is saturated.
5. The hydrogenated diene block copolymer according to Claim 4, wherein the block copolymer is a block copolymer represented by the general formula $[(A)-(B)]_n-X$, $[(A)-(B)-(C)]_n-X$ or $[(A)-(B)-(A)]_n-X$ wherein (A), (B) and (C) are as defined as in Claim 1, n is an integer of 2-4 and X is a coupling agent residue.
6. A modified hydrogenated diene block copolymer obtainable by modifying 100 parts by weight of a hydrogenated diene block copolymer according to Claim 4 with 0.01-20 parts by weight of an unsaturated compound having at least one functional group selected from the group consisting of acid anhydride group, carboxyl group, hydroxyl group, amino group and epoxy group.
7. A hydrogenated diene block copolymer composition comprising 1-99% by weight of at least one (modified) hydrogenated diene block copolymer (I) selected from the group consisting of the hydrogenated diene block copolymer according to Claim 1, the hydrogenated diene block copolymer according to Claim 2 and the modified hydrogenated diene block copolymer according to Claim 3 and 99-1% by weight of a non-polar resin (II), a polar resin (III) or both of (II) and (III) components.
8. A hydrogenated diene block copolymer composition comprising at least one (modified) hydrogenated diene block

copolymer (I) selected from the group consisting of the hydrogenated diene block copolymer according to Claim 1, the hydrogenated diene block copolymer according to Claim 2 and the modified hydrogenated diene block copolymer according to Claim 3, a polar resin (III) and 0.01-400 parts by weight, per 100 parts by weight of the total of the components (I) and (III), of a compatibilizing agent.

- 5 9. A hydrogenated diene block copolymer composition comprising the modified hydrogenated diene block copolymer (I) according to Claim 3 and a polar resin (III).
- 10 10. A hydrogenated diene block copolymer composition comprising 1-99% by weight of a hydrogenated diene copolymer (I) according to Claim 4 and 99-1% by weight of a non-polar resin (II), a polar resin (III) or both of (II) and (III) components.
- 15 11. A hydrogenated diene block copolymer composition comprising 1-99% by weight of a hydrogenated diene block copolymer (I) according to Claim 4, 99-1% by weight of a polar resin (III) and 0.01-400 parts by weight, per 100 parts by weight of the total of the components (I) and (III), of a compatibilizing agent.
- 20 12. A modified hydrogenated diene block copolymer composition comprising 1-99% by weight of a modified hydrogenated diene block copolymer (I) according to Claim 7 and 99-1% by weight of a non-polar resin (II), a polar resin (III) or both of (II) and (III) components.
- 25 13. A thermoplastic elastomer composition obtainable by melt-kneading, in the presence of a crosslinking agent, 10-90 parts by weight of a polyolefin resin (M) and 90-10 parts by weight of at least one (modified) hydrogenated diene block copolymer (N) selected from the group consisting of the hydrogenated diene block copolymer according to Claim 1, the hydrogenated diene block copolymer according to Claim 2 and the modified hydrogenated diene block copolymer according to Claim 3.
- 30 14. A thermoplastic resin composition comprising (a) 1-90% by weight of at least one (modified) hydrogenated diene block copolymer selected from the group consisting of the hydrogenated diene block copolymer according to Claim 1, the hydrogenated diene block copolymer according to Claim 2 and the modified hydrogenated diene block copolymer according to Claim 3, (b) 5-94% by weight of a thermoplastic polyester, a thermoplastic polyester elastomer or both of them and (c) 5-94% by weight of other thermoplastic polymer.
- 35 15. A thermoplastic resin composition comprising (a) 1-90% by weight of a (modified) hydrogenated diene block copolymer selected from the group consisting of the hydrogenated diene block copolymer according to Claim 1, the hydrogenated diene block copolymer according to Claim 2 and the modified hydrogenated diene block copolymer according to Claim 3, (b') 5-94% by weight of a thermoplastic polyamide, a thermoplastic polyamide elastomer or both of them and (c) 5-94% by weight of other thermoplastic polymer.
- 40 16. A thermoplastic resin composition comprising (a) 1-90% by weight of a (modified) hydrogenated diene block copolymer selected from the group consisting of the hydrogenated diene block copolymer according to Claim 1, the hydrogenated diene block copolymer according to Claim 2 and the modified hydrogenated diene block copolymer according to Claim 3, (b'') 5-94% by weight of a polyphenylene ether and (c) 5-94% by weight of other thermoplastic polymer.

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Patentansprüche

- 50 1. Hydriertes Dien-Blockcopolymer mit einem auf Polystyrol bezogenen zahlenmittleren Molekulargewichts von 50.000 bis 600.000, das ein Hydrierungsprodukt eines (A)-(B)-Blockcopolymerisats darstellt, in welchem (A) einen Polymerblock aus einer alkenyl-aromatischen Verbindung bedeutet und (B) einen statistischen Copolymerblock aus einer alkenyl-aromatischen Verbindung und einem konjugierten Dien bedeutet, worin der Vinylgehalt des konjugierten Dienanteils mehr als 60 % beträgt, oder eines (A)-(B)-(C)-Blockcopolymerisats, in welchem (A) und (B) wie oben definiert sind und (C) einen verlaufenden Copolymerblock aus einer alkenyl-aromatischen Verbindung und einem konjugierten Dien bedeutet, worin der Anteil der alkenyl-aromatischen Verbindung allmählich zunimmt, oder eines (A)-(B)-(A)-Blockcopolymerisats, in dem (A) und (B) wie oben definiert sind, wobei in dem Blockcopolymer

55 (1) das Gewichtsverhältnis der alkenyl-aromatischen Verbindung zum konjugierten Dien 5 : 95 bis 60 : 40

beträgt und

(2) der Gehalt der gebundenen alkenyl-aromatischen Verbindung in wenigstens einem Block (A) mindestens 3 Gewichts-% beträgt und der Gesamtgehalt der gebundenen alkenyl-aromatischen Verbindung in den zwei Blöcken (A) oder dem Block (A) und dem Block (C) 3 bis 50 Gewichts-%, bezogen auf die gesamten Monomeren, beträgt

und wobei im Hydrierungsprodukt mindestens 80 % der ungesättigten Doppelbindungen des konjugierten Dienanteils durch die Hydrierung abgesättigt sind.

- 10 2. Hydriertes Dien-Blockcopolymer nach Anspruch 1, wobei das Blockcopolymer ein Blockcopolymer ist, das durch die allgemeine Formel $[(A)-(B)]_n-X$, $[(A)-(B)-(C)]_n-X$ oder $[(A)-(B)-(A)]_n-X$ dargestellt wird, worin (A), (B) und (C) gleich wie in Anspruch 1 definiert sind, n eine ganze Zahl von 2 bis 4 ist und X der Rest eines Kupplungsmittels ist.
- 15 3. Modifiziertes hydriertes Dien-Blockcopolymer, erhältlich durch Umsetzen von 100 Gewichtsteilen des hydrierten Dien-Blockcopolymers nach Anspruch 1 oder 2 mit 0,01 bis 20 Gewichtsteilen einer ungesättigten Verbindung mit mindestens einer funktionellen Gruppe, ausgewählt aus der aus Säureanhydridgruppe, Carboxylgruppe, Hydroxylgruppe, Aminogruppe und Epoxygruppe bestehenden Gruppe.
- 20 4. Hydriertes Dien-Blockcopolymer mit einem auf Polystyrol bezogenen zahlenmittleren Molekulargewichts von 100.000 bis 600.000, das ein Hydrierungsprodukt eines (A)-(B)-Blockcopolymerisats darstellt, bestehend aus (A) einem Polymerblock einer alkenyl-aromatischen Verbindung und (B) einem statistischen Copolymerblock aus einer alkenyl-aromatischen Verbindung und einem konjugierten Dien, oder eines (A)-(B)-(C)-Blockcopolymerisats, bestehend aus dem Block (A), dem Block (B) und (C) einem Block eines verlaufenden Copolymerisats einer alkenyl-aromatischen Verbindung mit einem konjugierten Dien, worin der Anteil der alkenyl-aromatischen Verbindung allmählich zunimmt, oder eines (A)-(B)-(A)-Blockcopolymerisats, bestehend aus dem Block (A), dem Block (B) und dem Block (A), wobei in dem Blockcopolymer
 - 30 (1) das Gewichtsverhältnis der alkenyl-aromatischen Verbindung zum konjugierten Dien 5 bis 40 : 95 bis 60 beträgt,
 - (2) der Gesamtgehalt der gebundenen alkenyl-aromatischen Verbindung in dem Block (A) und dem Block (C) oder in den beiden Blöcken (A) 3 bis 25 Gewichts-%, bezogen auf die gesamten Monomeren, und der Gehalt der gebundenen alkenyl-aromatischen Verbindung in wenigstens einem Block (A) mindestens 3 Gewichts-% beträgt und
 - (3) der Vinylgehalt des konjugierten Dienanteils im Block (B) mehr als 60 % beträgt
- 35 5. Hydriertes Dien-Blockcopolymer nach Anspruch 4, wobei das Blockcopolymer ein Blockcopolymer ist, das durch die allgemeine Formel $[(A)-(B)]_n-X$, $[(A)-(B)-(C)]_n-X$ oder $[(A)-(B)-(A)]_n-X$ dargestellt wird, worin (A), (B) und (C) wie in Anspruch 1 definiert sind, n eine ganze Zahl von 2 bis 4 ist und X der Rest eines Kupplungsmittels ist.
- 40 6. Modifiziertes hydriertes Dien-Blockcopolymer, erhältlich durch Umsetzen von 100 Gewichtsteilen eines hydrierten Dien-Blockcopolymers nach Anspruch 4 mit 0,01 bis 20 Gewichtsteilen einer ungesättigten Verbindung mit mindestens einer funktionellen Gruppe, ausgewählt aus der aus Säureanhydridgruppe, Carboxylgruppe, Hydroxylgruppe, Aminogruppe und Epoxygruppe bestehenden Gruppe.
- 45 7. Zusammensetzung eines hydrierten Dien-Blockcopolymers, umfassend 1 bis 99 Gewichts-% mindestens eines (modifizierten) hydrierten Dien-Blockcopolymers (I), ausgewählt aus der aus dem hydrierten Dien-Blockcopolymer nach Anspruch 1, dem hydrierten Dien-Blockcopolymer nach Anspruch 2 und dem modifizierten hydrierten Dien-Blockcopolymer nach Anspruch 3 bestehenden Gruppe, und 99 bis 1 Gewichts-% eines unpolaren Harzes (II), eines polaren Harzes (III) oder beider Komponenten (II) und (III).
- 50 8. Zusammensetzung eines hydrierten Dien-Blockcopolymers, umfassend mindestens ein (modifiziertes) hydriertes Dien-Blockcopolymer (I), ausgewählt aus der aus dem hydrierten Dien-Blockcopolymer nach Anspruch 1, dem hydrierten Dien-Blockcopolymer nach Anspruch 2 und dem modifizierten hydrierten Dien-Blockcopolymer nach Anspruch 3 bestehenden Gruppe, ein polares Harz (III) und 0,01 bis 400 Gewichtsteile, pro 100 Gewichtsteile der Gesamtmenge der Komponenten (I) und (III), eines Verträglichkeitsvermittlers.

9. Zusammensetzung eines hydrierten Dien-Blockcopolymers, umfassend das modifizierte Dien-Blockcopolmer (I) nach Anspruch 3 und ein polares Harz (III).
- 5 10. Zusammensetzung eines hydrierten Dien-Blockcopolmers, umfassend 1 bis 99 Gewichts-% eines hydrierten Dien-Blockcopolymers (I) nach Anspruch 4 und 99 bis 1 Gewichts-% eines unpolaren Harzes (II), eines polaren Harzes (III) oder beider Komponenten (II) und (III).
- 10 11. Zusammensetzung eines hydrierten Dien-Blockcopolymers, umfassend 1 bis 99 Gewichts-% eines hydrierten Dien-Blockcopolymers (I) nach Anspruch 4, 99 bis 1 Gewichts-% eines polaren Harzes (III) und 0,01 bis 400 Gewichtsteile, pro 100 Gewichtsteile der Gesamtmenge der Komponenten (I) und (II), eines Verträglichkeitsvermittlers.
- 15 12. Zusammensetzung eines hydrierten Dien-Blockcopolymers, umfassend 1 bis 99 Gewichts-% eines hydrierten Dien-Blockcopolymers (I) nach Anspruch 7 und 99 bis 1 Gewichts-% eines unpolaren Harzes (II), eines polaren Harzes (III) oder beider Komponenten (II) und (III).
- 20 13. Thermoplastische Elastomer-Zusammensetzung, erhältlich durch Schmelzketten, in Gegenwart eines Vernetzungsmittels, von 10 bis 90 Gewichtsteilen eines Polyolefinharzes (M) und 90 bis 10 Gewichtsteilen mindestens eines (modifizierten) hydrierten Dien-Blockcopolymers (N), ausgewählt aus der Gruppe, die aus dem hydrierten Dien-Blockcopolymer nach Anspruch 1, dem hydrierten Dien-Blockcopolymer nach Anspruch 2 und dem modifizierten hydrierten Dien-Blockcopolymer nach Anspruch 3 besteht.
- 25 14. Thermoplastische Harz-Zusammensetzung, umfassend (a) 1 bis 90 Gewichts-% mindestens eines (modifizierten) hydrierten Dien-Blockcopolymers, ausgewählt aus der Gruppe, die aus dem hydrierten Dien-Blockcopolymer nach Anspruch 1, dem hydrierten Dien-Blockcopolymer nach Anspruch 2 und dem modifizierten hydrierten Dien-Blockcopolymer nach Anspruch 3 besteht, (b) 5 bis 94 Gewichts-% eines thermoplastischen Polyesters oder/und eines thermoplastischen Polyester-Elastomers und (c) 5 bis 94 Gewichts-% eines anderen thermoplastischen Polymers.
- 30 15. Thermoplastische Harz-Zusammensetzung, umfassend (a) 1 bis 90 Gewichts-% eines (modifizierten) hydrierten Dien-Blockcopolymers, ausgewählt aus der Gruppe, die aus dem hydrierten Dien-Blockcopolymer nach Anspruch 1, dem hydrierten Dien-Blockcopolymer nach Anspruch 2 und dem modifizierten hydrierten Dien-Blockcopolmer nach Anspruch 3 besteht, (b') 5 bis 94 Gewichts-% eines thermoplastischen Polyamids oder/und eines thermoplastischen Polyamid-Elastomers und (c) 5 bis 94 Gewichts-% eines anderen thermoplastischen Polymers.
- 35 16. Thermoplastische Harz-Zusammensetzung, umfassend (a) 1 bis 90 Gewichts-% eines (modifizierten) hydrierten Dien-Blockcopolymers, ausgewählt aus der Gruppe, die aus dem hydrierten Dien-Blockcopolymer nach Anspruch 1, dem hydrierten Dien-Blockcopolymer nach Anspruch 2 und dem modifizierten hydrierten Dien-Blockcopolymer nach Anspruch 3 besteht, (b") 5 bis 94 Gewichts-% eines Polyphenylenethers und (c) 5 bis 94 Gewichts-% eines anderen thermoplastischen Polymers.
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Revendications

1. Copolymère séquencé de diène hydrogéné ayant une masse moléculaire moyenne en nombre, réduite au polystyrène, de 50 000 à 600 000, qui est un produit d'hydrogénéation d'un copolymère séquencé (A)-(B) dans lequel (A) signifie une séquence polymère de composé alcényl-aromatique et (B) signifie une séquence copolymère statistique de diène conjugué et de composé alcényl-aromatique, dans laquelle la teneur en vinyle de la partie diène conjugué est supérieure à 60 %, d'un copolymère séquencé (A)-(B)-(C) dans lequel (A) et (B) ont les significations indiquées ci-dessus et (C) signifie une séquence à gradient de composition de copolymère de diène conjugué et de composé alcényl-aromatique dans laquelle la proportion du composé alcényl-aromatique augmente progressivement, ou d'un copolymère séquencé (A)-(B)-(A) dans lequel (A) et (B) ont les significations indiquées ci-dessus, copolymère séquencé dans lequel
- 45 (1) la proportion en poids du composé alcényl-aromatique au diène conjugué est de 5/95 à 60/40, et
(2) la teneur en le composé alcényl-aromatique lié dans au moins une séquence (A) est d'au moins 3 % en poids et le total des teneurs en composé alcényl-aromatique lié dans les deux séquences (A) ou dans la séquence (A) et la séquence (C) est de 3 à 50 % en poids par rapport au total des monomères,
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et dans lequel produit d'hydrogénéation au moins 80 % des insaturations à double liaison de la partie diène conjugué sont saturés par l'hydrogénéation.

5 2. Copolymère séquencé de diène hydrogéné selon la revendication 1, dans lequel le copolymère séquencé est un copolymère séquencé représenté par la formule générale $[(A)-(B)]_n-X$, $[(A)-(B)-(C)]_n-X$ ou $[(A)-(B)-(A)]_n-X$, où (A), (B) et (C) ont les mêmes définitions que dans la revendication 1, n est un entier de 2 à 4 et X est un résidu d'agent de couplage.

10 3. Copolymère séquencé de diène hydrogéné modifié, pouvant être obtenu par modification de 100 parties en poids du copolymère séquencé de diène hydrogéné selon la revendication 1 ou 2 avec 0,01 à 20 parties en poids d'un composé insaturé ayant au moins un groupe fonctionnel choisi dans l'ensemble constitué par un groupe anhydride d'acide, un groupe carboxy, un groupe hydroxy, un groupe amino et un groupe époxy.

15 4. Copolymère séquencé de diène hydrogéné ayant une masse moléculaire moyenne en nombre, réduite au polystyrène, de 100 000 à 600 000, qui est un produit d'hydrogénéation d'un copolymère séquencé (A)-(B) constitué de (A) une séquence polymère de composé alcényl-aromatique et (B) une séquence copolymère statistique de diène conjugué et de composé alcényl-aromatique, d'un copolymère séquencé (A)-(B)-(C) constitué de la séquence (A), de la séquence (B) et (C) d'une séquence à gradient de composition de copolymère de diène conjugué et de composé alcényl-aromatique dans laquelle la proportion du composé alcényl-aromatique augmente progressivement, ou d'un copolymère séquencé (A)-(B)-(A) constitué de la séquence (A), de la séquence (B) et de la séquence (A), copolymère séquencé dans lequel

- 20 (1) la proportion en poids du composé alcényl-aromatique au diène conjugué est de 5-40/95-60,
 25 (2) le total des teneurs en composé alcényl-aromatique lié dans la séquence (A) et la séquence (C) ou les deux séquences (A) est de 3 à 25 % en poids par rapport au total des monomères, et la teneur en le composé alcényl-aromatique lié dans au moins une séquence (A) est d'au moins 3 % en poids, et
 (3) la teneur en vinyle de la partie diène conjugué dans la séquence (B) est supérieure à 60 %,

30 et dans lequel copolymère d'hydrogénéation au moins 90 % des doubles liaisons de la partie diène conjugué sont saturés.

35 5. Copolymère séquencé de diène hydrogéné selon la revendication 4, dans lequel le copolymère séquencé est un copolymère séquencé représenté par la formule générale $[(A)-(B)]_n-X$, $[(A)-(B)-(C)]_n-X$ ou $[(A)-(B)-(A)]_n-X$, où (A), (B) et (C) ont les mêmes définitions que dans la revendication 1, n est un entier de 2 à 4 et X est un résidu d'agent de couplage.

40 6. Copolymère séquencé de diène hydrogéné modifié, pouvant être obtenu par modification de 100 parties en poids du copolymère séquencé de diène hydrogéné selon la revendication 4 avec 0,01 à 20 parties en poids d'un composé insaturé ayant au moins un groupe fonctionnel choisi dans l'ensemble constitué par un groupe anhydride d'acide, un groupe carboxy, un groupe hydroxy, un groupe amino et un groupe époxy.

45 7. Composition de copolymère séquencé de diène hydrogéné, comprenant 1 à 99 % en poids d'au moins un copolymère séquencé de diène hydrogéné (modifié) (I) choisi dans l'ensemble constitué par le copolymère séquencé de diène hydrogéné selon la revendication 1, le copolymère séquencé de diène hydrogéné selon la revendication 2 et le copolymère séquencé de diène hydrogéné modifié selon la revendication 3, et 99 à 1 % en poids d'une résine non polaire (II), d'une résine polaire (III) ou des deux composants (II) et (III).

50 8. Composition de copolymère séquencé de diène hydrogéné, comprenant au moins un copolymère séquencé de diène hydrogéné (modifié) (I) choisi dans l'ensemble constitué par le copolymère séquencé de diène hydrogéné selon la revendication 1, le copolymère séquencé de diène hydrogéné selon la revendication 2 et le copolymère séquencé de diène hydrogéné modifié selon la revendication 3, une résine polaire (III), et 0,01 à 400 parties en poids, pour 100 parties en poids du total des composants (I) et (III), d'un agent de compatibilité.

55 9. Composition de copolymère séquencé de diène hydrogéné, comprenant le copolymère séquencé de diène hydrogéné modifié (I) selon la revendication 3 et une résine polaire (III).

10. Composition de copolymère séquencé de diène hydrogéné, comprenant 1 à 99 % en poids d'un copolymère séquencé de diène hydrogéné (I) selon la revendication 4, et 99 à 1 % en poids d'une résine non polaire (II), d'une

résine polaire (III) ou des deux composants (II) et (III).

11. Composition de copolymère séquencé de diène hydrogéné, comprenant 1 à 99 % en poids d'un copolymère séquencé de diène hydrogéné (I) selon la revendication 4, 99 à 1 % en poids d'une résine polaire (III), et 0,01 à 400 parties en poids, pour 100 parties en poids du total des composants (I) et (III), d'un agent de compatibilité.

5 12. Composition de copolymère séquencé de diène hydrogéné modifié, comprenant 1 à 99 % en poids d'un copolymère séquencé de diène hydrogéné modifié (I) selon la revendication 7, et 99 à 1 % en poids d'une résine non polaire (II), d'une résine polaire (III) ou des deux composants (II) et (III).

10 13. Composition élastomère thermoplastique, pouvant être obtenue par malaxage à l'état fondu, en présence d'un agent de réticulation, de 10 à 90 parties en poids d'une résine de polyoléfine (M) et de 90 à 10 parties en poids d'au moins un copolymère séquencé de diène hydrogéné (modifié) (N) choisi dans l'ensemble constitué par le copolymère séquencé de diène hydrogéné selon la revendication 1, le copolymère séquencé de diène hydrogéné selon la revendication 2 et le copolymère séquencé de diène hydrogéné modifié selon la revendication 3.

15 14. Composition de résine thermoplastique, comprenant

20 (a) 1 à 90 % en poids d'au moins un copolymère séquencé de diène hydrogéné (modifié) choisi dans l'ensemble constitué par le copolymère séquencé de diène hydrogéné selon la revendication 1, le copolymère séquencé de diène hydrogéné selon la revendication 2 et le copolymère séquencé de diène hydrogéné modifié selon la revendication 3,

(b) 5 à 94 % en poids d'un polyester thermoplastique, d'un élastomère de polyester thermoplastique ou des deux, et

25 (c) 5 à 94 % en poids d'un autre polymère thermoplastique.

15. Composition de résine thermoplastique, comprenant

30 (a) 1 à 90 % en poids d'un copolymère séquencé de diène hydrogéné (modifié) choisi dans l'ensemble constitué par le copolymère séquencé de diène hydrogéné selon la revendication 1, le copolymère séquencé de diène hydrogéné selon la revendication 2 et le copolymère séquencé de diène hydrogéné modifié selon la revendication 3,

(b') 5 à 94 % en poids d'un polyamide thermoplastique, d'un élastomère de polyamide thermoplastique ou des deux, et

35 (c) 5 à 94 % en poids d'un autre polymère thermoplastique.

16. Composition de résine thermoplastique, comprenant

40 (a) 1 à 90 % en poids d'un copolymère séquencé de diène hydrogéné (modifié) choisi dans l'ensemble constitué par le copolymère séquencé de diène hydrogéné selon la revendication 1, le copolymère séquencé de diène hydrogéné selon la revendication 2 et le copolymère séquencé de diène hydrogéné modifié selon la revendication 3,

(b") 5 à 94 % en poids d'un poly(phénylène-éther), et

45 (c) 5 à 94 % en poids d'un autre polymère thermoplastique.